

EFFECT OF GRAVITY ON POROUS TRICALCIUM PHOSPHATE AND NONSTOICHIOMETRIC TITANIUM CARBIDE PRODUCED VIA COMBUSTION SYNTHESIS

M. Castillo, J. J. Moore, F.D. Schowengerdt, R.A. Ayers

Center for Commercial Applications of Combustion in Space (CCACS), Colorado School of Mines, 1500 Illinois St., Golden, Colorado 80401, USA

ABSTRACT

Novel processing techniques, such as self-propagating high temperature synthesis (SHS), have the capability to rapidly produce advanced porous materials that are difficult to fabricate by other methods. This processing technique is also capable of near net shape synthesis, while variable gravity allows the manipulation of the structure and composition of the material. The creation of porous tricalcium phosphate (TCP) is advantageous in the biomaterials field, since it is both a biocompatible material and an osteoconductive material. Porous tricalcium phosphate produced via SHS is an excellent candidate for bone scaffold material in the bone regeneration process. The porosity allows for great vascularization and ingrowth of tissue. Titanium Carbide is a nonstoichiometric biocompatible material that can be incorporated into a TiC-Ti composite system using combustion synthesis. The TiC-Ti composite exhibits a wide range of mechanical and chemical properties. Both of these material systems (TCP and TiC-Ti) can be used to advantage in designing novel bone replacement materials. Gravity plays an important role in both the pore structure and the chemical uniformity of these composite systems and offers considerable potential in advanced bone engineering.

INTRODUCTION

New and novel bone replacement materials are currently being investigated at the Colorado School of Mines through the process of self-propagating high temperature synthesis (SHS). SHS with its rapid kinetics allows the production of near net-shaped samples. This process is highly exothermic and can allow for difficult intermetallic and porous materials to easily be manufactured. The processing parameters include green density, gasifying agents, reaction stoichiometry, and gravity. Green density is the initial density of the reactants and allows for control over the final apparent porosity. Gasifying agents also allow for the generation of additional pores. Gasifying agents are selected so that they evolve and do not contaminate the sample or change the desired final stoichiometry of the products. Reaction stoichiometry controls the combustion temperature and the final composition of the sample. Furthermore, the final composition can be graded from the reaction stoichiometry. Gravity plays a role in the morphology of the pores and final graded structure. SHS performed in microgravity will affect samples that are sensitive to cooling rates. The samples manufactured in microgravity experience heat loss only through radiation since convection is lost. The addition of gravity will affect samples that have a liquid-solid reaction through gravity-driven fluid flow (in terrestrial conditions). All SHS processing parameters focus on the control of porosity and composition, which are critical when designing a biomaterial.

The current state of the art bone implants are in dire need of improved design and functionality. Current implants lack mechanical properties that match the properties of bone.

The production of porous implants will lead to a more graded implant in-vivo that will be engineered to grade the mechanical properties of the bone with those of the implant and thereby reduce the occurrence of stress shielding. Peters et al. have recently discussed the possibility of combining materials and properties to make functionally graded materials in order to improve implant material [1].

In those cases in which it may not be necessary to match the mechanical properties of the bone, a porous resorbable material can be used as the alternative. Porous resorbable materials provide a scaffold onto which the bone can remodel and resorb. An optimum level of porosity allows for easy vascularization and infiltration of tissue into the pores. Although this latter resorbable scaffold may lack the necessary mechanical properties required of an implant, this problem can be overcome with external devices that maintain the integrity of the injured area during the bone remodeling process.

EXPERIMENTAL PROCEDURE

SHS is conducted by mixing the reactants in the desired reaction stoichiometry for 8 hours to ensure thorough mixing. Prior to mixing, temperature-enthalpy calculations are performed to determine the adiabatic temperature for the reaction [2]. The adiabatic temperature is the maximum achievable theoretical temperature generated in the SHS reaction with no heat loss from the system. The TCP system requires that all processing be performed in an inert atmosphere (i.e. glovebox). TCP is created by mixing and reacting calcium oxide (CaO) and phosphorus pentoxide (P₂O₅), - a highly hygroscopic material. The mixtures are either pressed to a desired relative green density or poured into a paper mold as a loose powder mixture, depending on the desired green density. Each sample is reacted in an inert atmosphere and the reaction is initiated via a tungsten resistance coil at the bottom of the sample, with the propagation wave traveling upwards. Samples are made into cylinders that have a height of 2.54 cm and a diameter of 1.27 cm (2:1 aspect ratio). Physical data for the reactant powders are listed in Table 1:

Table 1. Physical data for the reactant powders.

	CaO	P ₂ O ₅	Ti	C
Particulate Size (µm)	<45	<94	<45	<45
Purity (%)	99.99	99.9	99.998	99.5
Melting Point (°C)	2888		1660	
Sublimation Point (°C)		631		3652 - 3697
Molecular Mass (g/mol)	56.07	141.92	47.87	12.01

All microgravity experiments were conducted aboard the NASA KC-135 low-G flight research aircraft in parabolic flight patterns that typically achieve ~15-20 seconds of low gravity and ~20 seconds of high (2G) gravity. A special flight rack (COSYM) was used to conduct the experiments and to obtain the experimental data (i.e. video, temperature, pressure). The reacted products were characterized using a Philips Quanta 600 environmental SEM. Apparent porosity measurements were conducted according to ASTM Designation C20-92.

RESULTS AND DISCUSSION

XRD analysis confirmed that the alpha phase of tricalcium phosphate had been produced via SHS. Shown below in Figure 1 (A), the scanning electron microscope (SEM) photomicrograph exhibits the highly porous morphology of the SHS-produced TCP. Typical bone exhibits a bimodal distribution of pores in which the finer pores range from 100-300 microns and the larger ones are on the order of millimeters. The SHS produced TCP exhibits both ranges of pores. Figure 1 (B) shows TCP produced aboard the NASA KC-135 (low-G flight) while the Figure 1 (C) shows TCP produced under terrestrial conditions (1G). SHS of TCP in microgravity displays typical hexagonal type grain growth and the lack of gravity allows nuclei to be unrestrained. TCP produced in terrestrial conditions exhibits lamellar type growth, where gravity dictates the pattern or direction of lamellar grains. The characteristic spots shown in Figure 1 (C) were determined by Valdés et al. to be calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$) quenched at the surface [3].

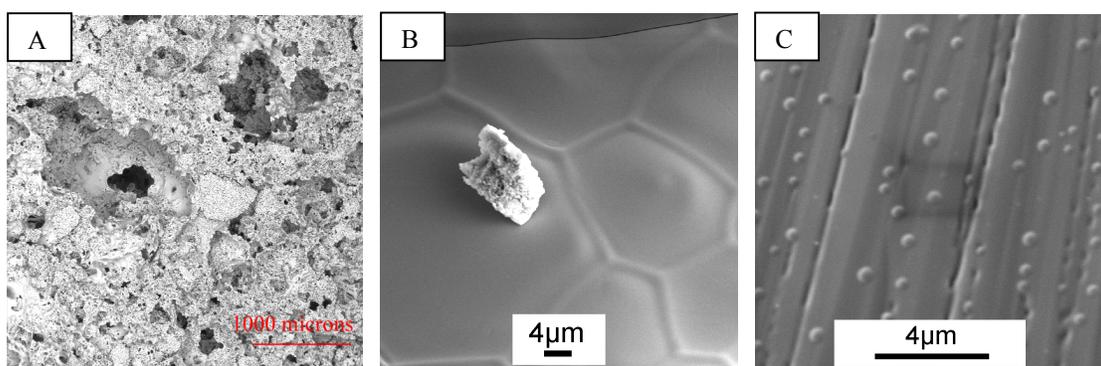


Figure 1. SEM photomicrograph of SHS produced TCP. A and C are manufactured in terrestrial conditions and B is produced aboard the NASA KC-135 (low-G plane).

SHS was conducted on TiC type materials under terrestrial conditions at the Colorado School of Mines. The SHS reactant system studied is $(1+x)\text{Ti} + \text{C}$, where $x = 0, 0.5, 1.0,$ and 1.5 . Reactions that are able to propagate are shown below in the Table 2. Due to the high thermal conductivity of the reactants, this system is able to react in relatively loose powder conditions that generates a 30% relative green density. Higher relative green densities would not sustain the SHS reaction in propagating mode due to heat being dissipated too rapidly from the combustion front.

Table 2. Successful SHS reactant combinations for the TiC_x system.

x	Relative Green Density			
	30%	40%	45%	50%
0.0	X	X	X	X
0.5	X	X	X	
1.0	X	X		
1.5	X			

It has been shown from previous research that these reactant combinations have the potential to produce nonstoichiometric TiC_x [2]. The phase diagram for TiC shows a homogeneous region where TiC_x can be produced in the range of $0.47 \leq x \leq 1.0$ [3]. The composition of the SHS-produced TiC is currently under investigation to produce evidence of nonstoichiometric titanium

carbide and the possibility of a gravity-driven, functionally graded material (FGM). There is a significant amount of liquid Ti formed during the reaction and it may be expected to see a gradient of Ti that would settle towards the bottom of the sample due to gravity.

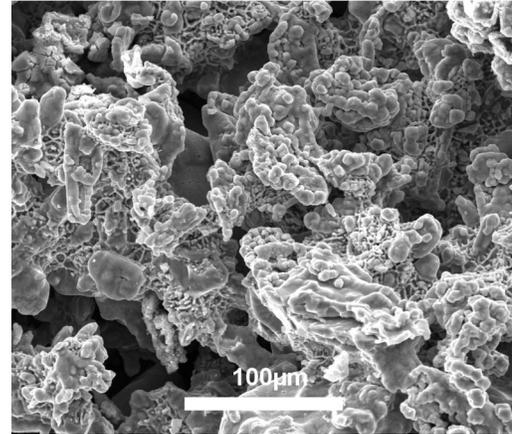
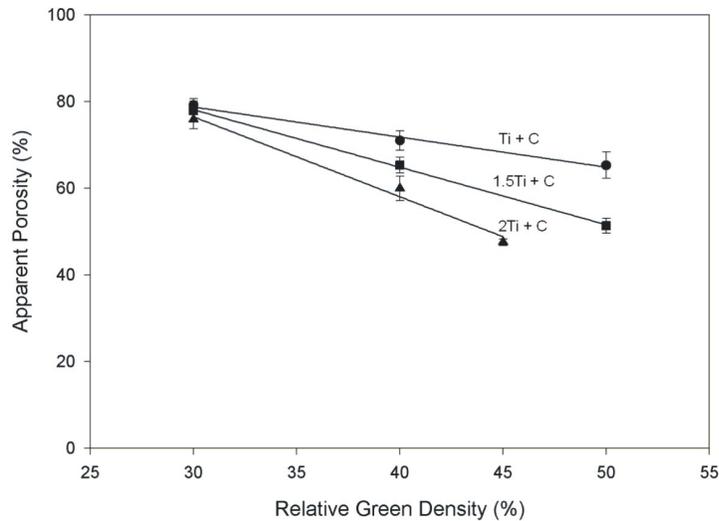


Figure 2. Relative green density vs. apparent porosity for the TiC reactions.

Figure 3. SEM photomicrograph of the reaction 2.5Ti + C

Figure 2 shows how relative green density can affect the apparent porosity of the final sample. When designing an implant, careful considerations involving porosity and distribution of pores are critical. This analysis provides a means of designing a porous FGM implant in which the porosity gradient can be tailored to meet both mechanical property and bone growth requirements.

The SEM photomicrograph shown in Figure 3 exhibits the porous microstructure of these materials. This photomicrograph is for the 2.5Ti + C reaction (30% relative green density) and has a porosity that fits into the range of that in natural bone. There are very fine micro and nano size pores that are not visible in the photomicrograph. A detailed analysis of the composition of the material may result in surface compositions that are conducive to osseointegration with the implant material.

REFERENCES

- 1.0 F. M. Peters, C. Schiller, M. Siedler, Functionally graded materials of biodegradable polyesters and bonelike calcium phosphate for bone replacement, *Functionally Graded Materials 2000*, Ceramic Transactions, 114, (2000) p. 97-107.
- 2.0 J. J. Moore, An examination of the thermochemistry of combustion synthesis reactions, *Processing and Fabrication of Advanced Materials III*, The Minerals, Metals & Materials Society, (1994) p. 817-831.
- 3.0 V. P. Gortcheva, , G. R. Morales, J. J. P. Valdés, et al., Fibrous growth of tricalcium phosphate ceramics, *J. of Mat. Sci.: Mat. in Medicine*, 8, (1997) p. 297-301.
- 4.0 Z. A. Munir, J. B. Holt, Combustion synthesis of titanium carbide theory and experiment, *J. of Mat. Sci.*, 21, (1986) 251-259.
- 5.0 E. K. Storms, *The refractory carbides*, Academic Press, New York, (1967) p. 3.